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KINETICS AND MECHANISMS OF THERMOLYTIC INTERCONVERSIONS 1/1  
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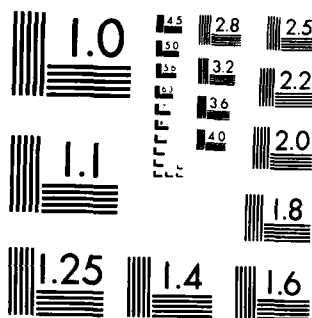
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KINETICS AND MECHANISMS OF THERMOLYTIC  
INTERCONVERSIONS OF BORON HYDRIDES

Final Technical Report

by

R. Greatrex, N.N. Greenwood, and G.A. Jump

June, 1984

United States Army  
RESEARCH & STANDARDIZATION GROUP (EUROPE)  
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## Abstract

A Mass-spectrometric method for following the kinetics of decomposition and interconversion of the boron hydrides in the gas phase has been perfected. All volatile components of the reacting mixture, including  $H_2$ , can be analyzed quantitatively and continuously.

Gaseous hexaborane(10) has been studied by this method for pressures in the range 1-10 mmHg, and at temperatures between 75 and 165°C. Its decomposition is much slower than implied in the literature, ~~and follows second-order kinetics with an activation energy of  $79.7 \pm 3.7$  kJ mol<sup>-1</sup>.~~ The main products are hydrogen and a non-volatile solid, together with minor amounts of  $B_5H_9$  and  $B_{10}H_{14}$ . Added hydrogen has little effect on the initial rates. Initially, one mole of  $H_2$  is produced for each mole of  $B_6H_{10}$  consumed but this gradually rises to  $2H_2$  per  $B_6H_{10}$ . A plausible mechanism is proposed to account for these observations.

Preliminary work suggests that the slow room-temperature decomposition of liquid  $B_6H_{10}$  may be related to that in the gas phase, whereas reactions under hot/cold conditions (e.g. 200°C/0°C) follow a different course leading to the macropolyhedral species  $B_{13}H_{19}$ ,  $B_{15}H_{23}$ , and other higher boranes, in preference to ill-defined polymeric solids. Other preliminary experiments show that, although gaseous  $B_6H_{10}$  does not exchange with  $D_2$  in a clean vessel at room temperature, exchange does occur in vessels coated with polymeric borane deposits; this provides a convenient route to hexaborane(10) deuterated preferentially at the terminal basal sites.

In a parallel study, direct and rapid exchange has been established between  $D_2$  and  $B_4H_{10}$  in the gas phase; this resolves a troublesome inconsistency in the literature and strengthens the view that the equilibrium  $B_4H_{10} \rightleftharpoons \{B_4H_8\} + H_2$  is of major importance both in the thermal decomposition of  $B_4H_{10}$  and in borane interconversion reactions generally.

Keywords

Hexaborane(10), Tetraborane(10)  
Borane Thermolysis  
Quantitative Mass Spectrometry  
Viscous-Flow Sampling  
Isotope-Exchange (D/H)  
Ion-Molecule Formation  
Gas-phase Kinetics

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## Personnel

*Mr G.A. Jump*, who was supported directly by the grant during the period October 1980-September 1983, successfully defended his PhD Thesis entitled "An Investigation of the Gas-Phase Thermolysis of Hexaborane(10) by Quantitative Mass Spectrometry" in June 1984. A copy of the thesis is included in this Final Report as Appendix 1. *Dr Ann Woollins* was employed on a part-time basis, with support from grant funds, to help with the synthesis of boranes and other essential intermediates.

Other people not directly supported by the Grant but actively involved throughout the work were the Principal Investigator *Professor N.N. Greenwood*, the Assistant Investigator *Dr R. Greatrex*, and an Experimental Officer, *Mr D. Singh*.

## General Introduction

Virtually all routes to the higher boranes involve, at some stage, the pyrolysis of diborane and the concurrent thermolytic interconversion of the various intermediate boron hydrides. These reactions are numerous and complex and there is a formidable literature on the subject.<sup>1-4</sup> Despite this, many aspects are unclear and there is controversy on nearly every proposed step in the sequence of reactions by which  $B_2H_6$  converts into  $B_4H_{10}$ ,  $B_5H_9$ ,  $B_5H_{11}$ ,  $B_6H_{10}$ ,  $B_6H_{12}$ ,  $B_8H_{12}$ ,  $B_9H_{15}$ , and  $B_{10}H_{14}$ . Progress has been hampered not only by the complexity of the system and the great reactivity of the boranes and their fragments, but also by the great difficulty of analysing the gas mixtures at various stages of the reaction.

We recently described a new approach to this important problem<sup>5</sup> which offered the exciting prospect that major advances could be made in our understanding of this intriguing system. In brief, the method involved sampling the thermostatted reaction mixture at appropriate time intervals by bleeding it directly into an MS30 mass spectrometer and recording the spectrum. The intensity of each line in the spectrum was measured and the whole was then fitted by a least-squares computer programme using the previously measured standard mass spectra of all the component boranes. With appropriate calibration procedure this gave a detailed instantaneous product analysis of the progress of the reaction without disturbing the bulk of the reaction mixture.

In this report we describe further development and refinement of this basic method and its extension to include the simultaneous analysis of hydrogen in these systems. We then go on to discuss a detailed kinetic study of the thermolysis of pure hexaborane(10), together with some related studies on this borane. This work is described in more detail in the Ph.D. Thesis of Mr G.A. Jump,<sup>6</sup> which has recently been successfully defended, and in a paper which has been submitted for publication.<sup>7</sup> Copies of these documents are included as Appendixes 1 and 2 in this report. Though not supported directly by the present Grant, cognate work involving a study of the exchange of deuterium with tetraborane(10) is also outlined. The full paper describing this work is in the press,<sup>8</sup> and a copy is also included (Appendix 3).

## Experimental Section

**Materials.**— The boranes  $B_2H_6$ ,  $B_4H_{10}$ , and  $B_6H_{10}$  were prepared by methods described in the literature<sup>9-11</sup> and purified by standard grease-free vacuum-line techniques.  $B_5H_9$  was provided by courtesy of Dr R.E. Williams, Chemical Systems Inc., California, and  $B_{10}H_{14}$  was a commercial sample (Olin Chemicals Co. Ltd.), sublimed before use. CP Grade hydrogen and helium, Standard Grade argon, and Research Grade krypton were obtained from BOC Ltd., and deuterium from Argo International Ltd., all were used without further purification. A high-integrity glove box (Mark 4B) from Faircrest Engineering was used in the handling of air- and moisture-sensitive solids and solutions. This was equipped with a gas recirculation and purification set for continuous operation at moisture levels of typically 5 ppm and oxygen levels of less than 1 ppm (monitored, respectively, with a Simac mini-Aquanel and an Oxanal meter). All these items were purchased during the Grant period using University Departmental funds.

**Instrumentation.**— The progress of each reaction was followed by two mass spectrometers: a Kratos MS30 double-beam instrument to monitor the boranes, and a smaller MS10 to analyze quantitatively for dihydrogen. The MS30 was equipped with a DS55 data-acquisition system consisting of a NOVA 3 minicomputer coupled with a Phoenix Disk Drive, model 6050, both from Data General Ltd. Operation was through a Hewlett Packard HP2623A graphics terminal. The NOVA 3 was linked by direct line to the University's central Amdahl VM/470 computer which houses the suite of programmes used in the data analysis. Installation

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of the data-acquisition facilities was carried out entirely during the Grant period and was financed entirely from University Departmental funds.

Mass-Spectrometric Methods of Analysis.- Development of a Novel Viscous-Flow Sampling Method. The methods of analysis used in this work have developed out of the earlier efforts in this laboratory to devise a technique for the continuous sampling of borane/hydrogen mixtures.<sup>5</sup> However, the need to obtain reliable quantitative data from which precise kinetic parameters can be determined, has necessitated a fundamental reappraisal of the method of sampling and calibration. It can be shown<sup>6</sup> by a detailed consideration of the (predominantly viscous) flow through the sampling capillaries that the procedure adopted in the earlier exploratory work, of using the response of one gas (i.e. argon) in the mixture to correct the response of another, is likely to cause an automatic error in the calculated response of the second gas. Moreover, the effects are likely to be exacerbated in reactions in which dihydrogen is produced, because of its low viscosity and molecular weight.

Ideally, a method of sampling was required in which the components of the mixture would flow independently of one another, such that the calibration curves of total ion current vs. partial pressure for the individual boranes would remain invariant to changes in the mixture. We therefore explored, in some detail, batch sampling methods employing molecular flow through the capillaries, but these proved unsuccessful because of insurmountable problems associated with adsorption of the boranes on the walls of the sampling reservoir and other parts of the system at the low pressures required ( $\sim 10^{-2}$  mmHg).

Being obliged to resort to viscous flow, we sought other means of ensuring that the calibration curves would be unaffected by changes in the mixture. We achieved this by including a large background pressure of an inert gas in each mixture, both in the calibration procedure and in the actual thermolysis experiments. The purpose of this added gas is to reduce the variability of viscosity and the effects due to changes in total pressure in the reaction mixture to a level which is negligible compared with other probable experimental errors. Helium, which has a low efficiency as a kinetic third body, was chosen for this purpose, and pressures of ca. 100 mmHg were found to be adequate. A feature of this method is that the rate of flow of any particular component through the sampling capillaries, and therefore the response of the spectrometer to that component, is predicted (for the relatively low partial pressures of 0-10 mmHg employed in this work) to be approximately linearly related to its partial pressure in the mixture, and this expectation is realized in practice in the new calibration curves.

Calibration Procedure and Data Analysis. Two types of information are required in order to analyze the spectrum of a mixture: (a) calibrations of spectrometer response versus partial pressure in the reaction vessel for each component, (b) mass spectral profiles, under standard source conditions, for each borane. A known partial pressure of argon was included in each calibration and reaction mixture to act as a standard, so that correction could be made for changes in spectrometer performance and sensitivity. Further technical details are in Appendixes 1 and 2.

Analysis of Hydrogen. The development of a means of measuring dihydrogen quantitatively and continuously, in parallel with the boranes in these mixtures, is a major feature of this work. This has been achieved by introducing an additional capillary leak from the reaction vessel to a second dedicated mass spectrometer. The capillary was connected to the MS10 by glass tubing of internal diameter 8 mm and length 11 m. A helical trap of total length 6.6 m was included in this line to remove boranes, thereby ensuring that the signal at m/z 2 contained no contribution from hydrogen ions produced by borane

fragmentation. This procedure also avoided contamination of the MS10 source and resulted in remarkably stable operating conditions and greatly extended source lifetime. The trap is capable of removing even  $B_2H_6$ , despite the fact that this borane has a vapour pressure of ca.  $10^{-4}$  mmHg at the temperature of liquid nitrogen. This is presumably due to cryoadsorption on the walls of the glass spiral, and care had to be taken to ensure that excessive quantities of condensed material did not accumulate, otherwise the true vapour pressure was eventually established and the borane passed through.

The arguments presented earlier concerning flow in the capillaries are generally applicable to the analysis of boranes on the MS30 and hydrogen on the MS10. The calibration procedure for hydrogen was essentially the same as that for the boranes; again, full details can be found in Appendixes 1 and 2.

Thermolysis Procedure.— The gas mixtures were prepared in calibrated bulbs on a vacuum line fitted with HP Rotoflo greaseless taps. Pressure measurement was by mercury manometer. The mixtures were then expanded slowly into a pyrex reaction vessel (volume ca.  $1\text{ dm}^3$ ) enclosed in a thermostatted oven at the required temperature (see Appendix 2 for details of temperature control and measurement), and this was taken as the zero reaction time. Samples were admitted without delay into the two mass spectrometers via separate 180 mm lengths of 0.1 mm diameter Veridia tubing, and scanning was initiated immediately. Approximately 1 minute later the reaction vessel was isolated from the vacuum line by means of a long-distance-control, greaseless tap (J. Young Scientific Glassware Ltd.), the handle of which protruded through the base of the insulated oven. A similar tap, with a capillary sidearm to reduce dead-space, allowed the flow of sample to the mass spectrometer to be interrupted, so that slow reactions could be monitored periodically rather than continuously.

#### A Kinetic Study of the Gas-Phase Thermolysis of Hexaborane(10)

Introduction.— A particularly intriguing aspect of the thermolysis of diborane(6) is the virtual absence of hexaboranes and other species intermediate between the pentaboranes and  $B_{10}H_{14}$  in this complex interacting system. Schaeffer<sup>12</sup> has suggested that the Lewis base properties of  $B_6H_{10}$ , as revealed in its recent chemistry,<sup>13-16</sup> provide a likely explanation for this apparent anomaly, and has further suggested that this borane may play a crucial role in the pyrolysis process by virtue of its propensity to react with acidic borane intermediates such as  $\{BH_3\}$ ,  $\{B_3H_7\}$ ,  $\{B_4H_8\}$ ,  $B_8H_{12}$ , and  $\{B_9H_{13}\}$ .†

Surprisingly little work has been done on  $B_6H_{10}$ , and none of it is of a kinetic nature. The early experiments of Stock<sup>17</sup> and the more recent pyrolysis studies of Schaeffer and co-workers<sup>15</sup> were carried out mainly on liquid samples, and the results may not therefore be directly relevant to events in the gas phase. Some preliminary gas-phase work was reported from this laboratory<sup>5</sup> but the sample used is now known to have been impure.

To assess the role of  $B_6H_{10}$  in the thermolysis of  $B_2H_6$  we plan to carry out a systematic study of cothermolysis reactions of  $B_6H_{10}$  with other boranes in the gas phase. As a precursor to this we have made a detailed kinetic study of the thermolysis of pure  $B_6H_{10}$ .

Results and Discussion.— Main Features. Pure  $B_6H_{10}$  was found to be surprisingly stable in the gas phase. At a pressure of 3.5 mmHg no significant decomposition was detected over a period of 24 hours at 348 K. At 393 K the pure sample

†Throughout this Report curly brackets {} are used to denote non-isolable reactive species.

decomposed slowly to yield mainly hydrogen, together with very small amounts of  $B_5H_9$  and  $B_{10}H_{14}$  in an approximate molar ratio of 5:1 as the only stable volatile products:  $B_2H_6$  was detected only in trace amounts and did not accumulate. Most of the boron (ca. 90%) disappeared entirely from the gas phase and was deposited predominantly on the lower walls of the vessel as a yellowish solid hydride. At higher temperatures there was no significant change in the product distribution but the faster rate of reaction resulted in more stable operating conditions and a consequent improvement in the quality of the borane data. A typical reaction profile at 426 K is shown in Figure 1.

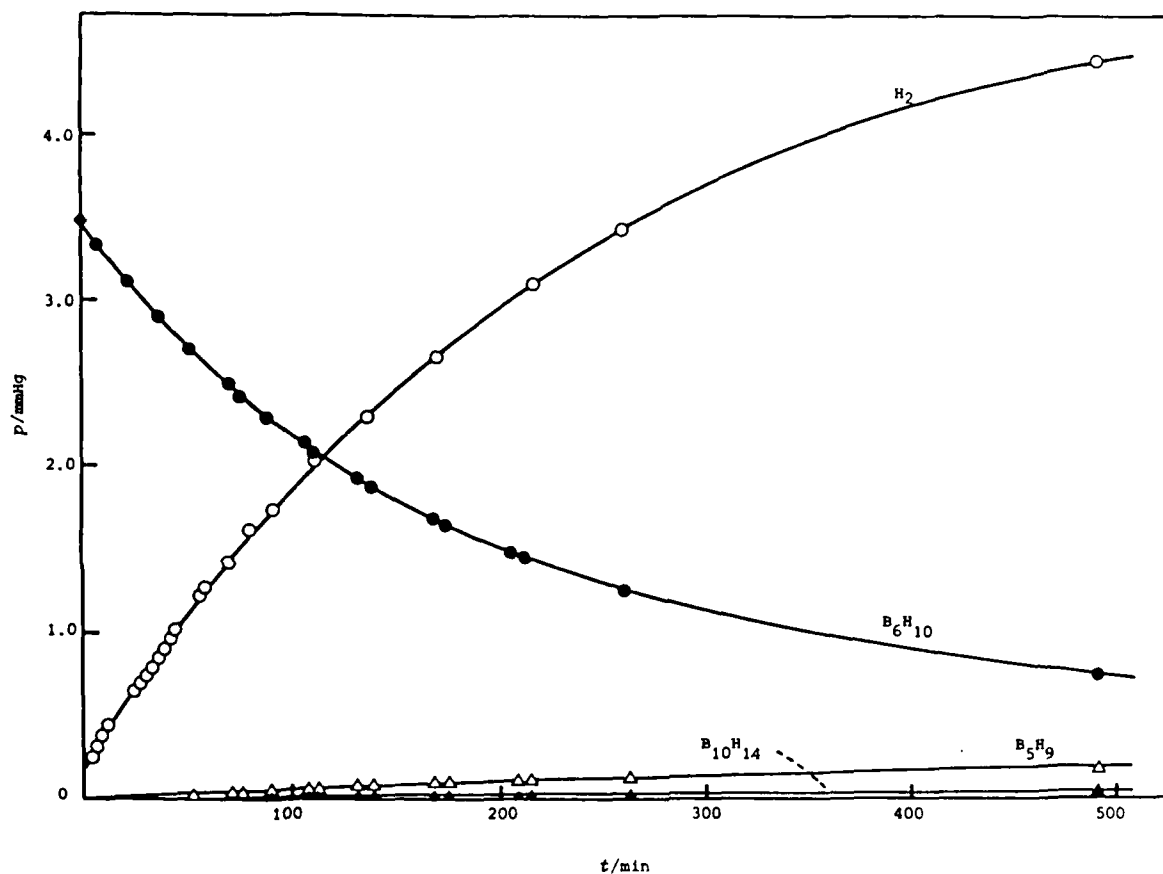


Figure 1. Reaction profile for thermolysis of  $B_6H_{10}$  ( $p_0 = 3.51$  mmHg) at 426 K

In the early stages of thermolyses at lower temperatures (e.g. 373 K) weak borane-like peaks were seen in the mass spectrum in the region  $m/z$  90-100, with a base peak at  $m/z$  93, indicative <sup>18</sup> of  $B_8H_{12}$ . The intensity of these peaks decreased as the reaction proceeded and they were eventually lost under the  $B_8$  and  $B_9$  envelopes of the fragmenting  $B_{10}H_{14}$ . Later in the reaction  $B_{13}$ ,  $B_{14}$ , and  $B_{15}$  species were observed, though at barely detectable levels. In an experiment at 333 K designed to look specifically for reactive intermediates in the early stages of the decomposition, a sample of  $B_6H_{10}$  was held at a much higher pressure (23.2 mmHg) and monitored at very high gain on the mass spectrometer. Under these conditions peaks in the region  $m/z$  100-110, characteristic <sup>18</sup> of  $B_9H_{15}$ , were also observed, at one stage in greater intensity than those in the  $B_8$  region. An interesting  $B_{12}$  species was also detected, but this was subsequently shown to be the result of an ion-molecule reaction in the source of the mass spectrometer (see Appendix 2 for details).

**Reaction Stoichiometry and Kinetic Parameters.**— From a careful study of initial rates of hydrogen production and  $B_6H_{10}$  consumption over a range of temperatures and pressures, the thermolytic decomposition of  $B_6H_{10}$  in the gas phase at low pressures has been shown to proceed with second-order kinetics and an activation energy of  $79.7 \pm 3.7 \text{ kJ mol}^{-1}$ . The main experimental results are summarized in Figures 2 and 3: full details are in Appendixes 1 and 2.

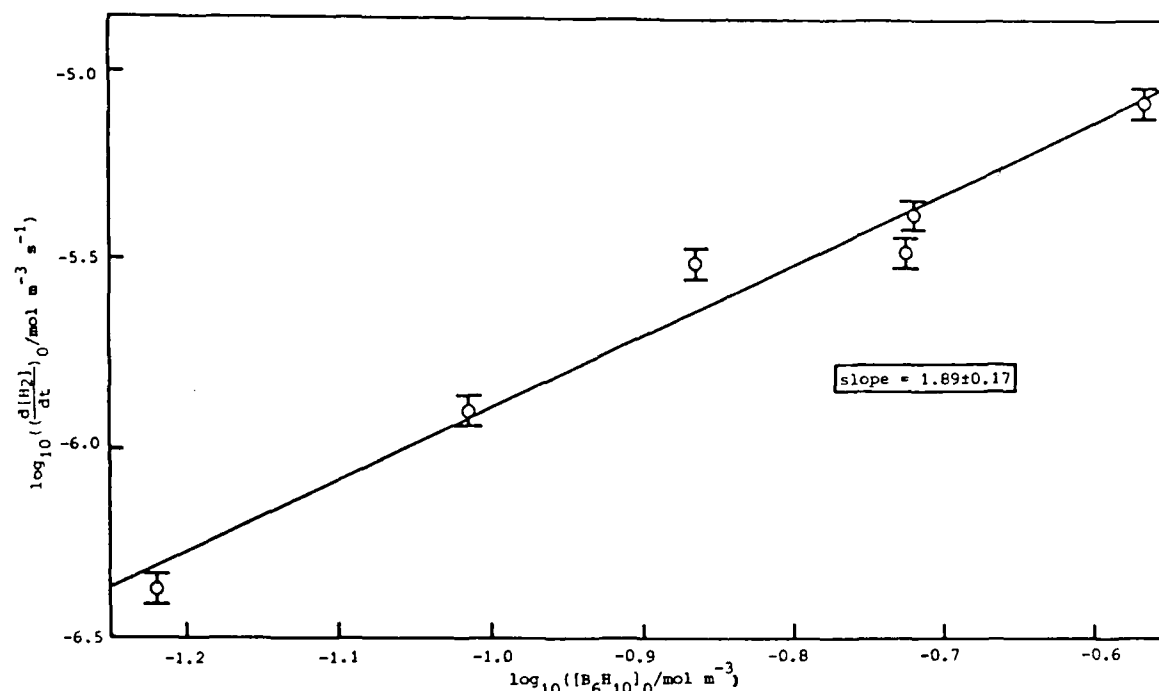


Figure 2. Plot of the log of the initial rate of hydrogen production versus the log of the initial concentration of  $B_6H_{10}$ , showing the reaction to be second order.

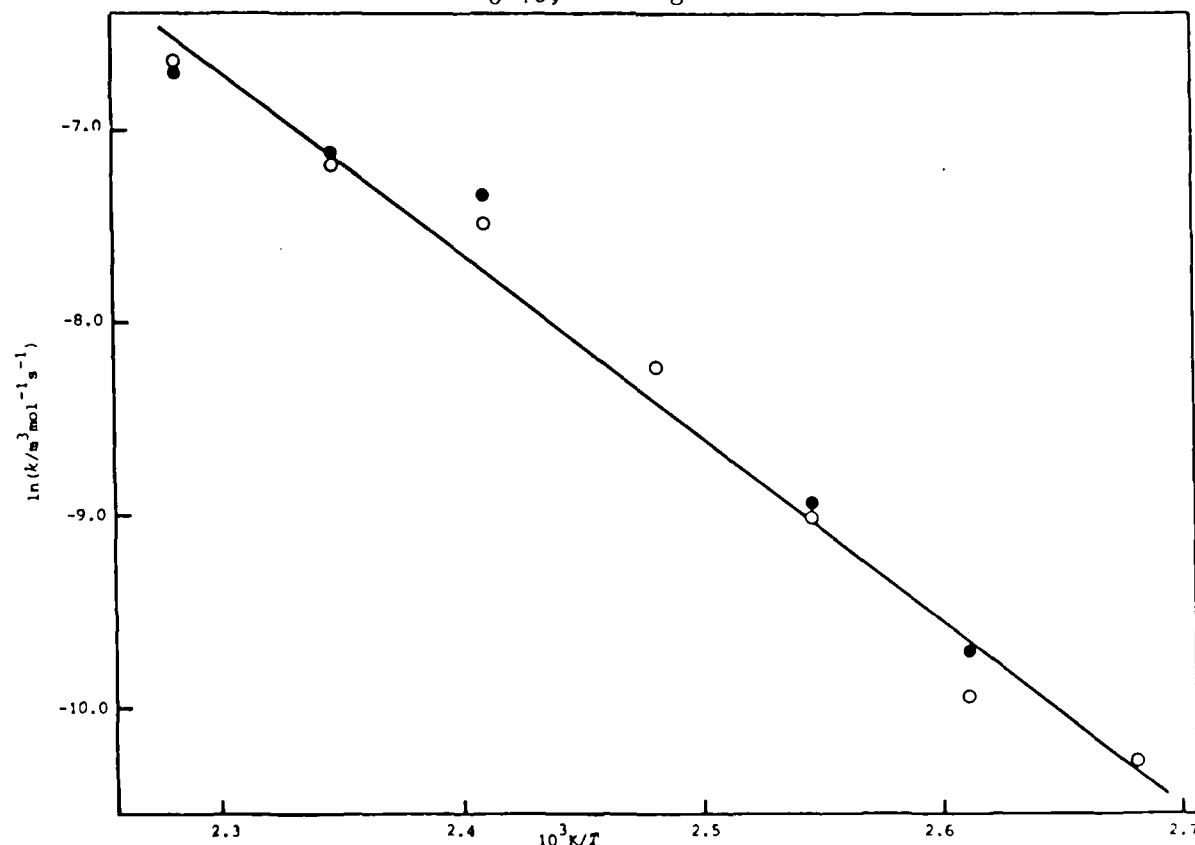


Figure 3. Arrhenius plot for the thermolysis of  $B_6H_{10}$  at constant concentration ( $0.134 \text{ mol m}^{-3}$ ). Open circles refer to the hydrogen data and solid circles to the borane data. The line drawn through the data represents the best fit to the hydrogen data; the line of best fit to the borane data is virtually coincident

In the initial stages the reaction produces one mole of hydrogen per mole of  $B_6H_{10}$  consumed, and deposits some 90% of the reacted borane from the gas phase as a non-volatile solid hydride of approximate composition  $BH_{1.33}$ , which then loses more hydrogen to give a solid of composition  $BH_{1.0}$ .

The Effect of Added Hydrogen.— Second-order plots of the  $B_6H_{10}$  data (typified by that in Figure 1) are linear over at least two half-lives (see Figure 4), implying that there is no significant interference from products, including

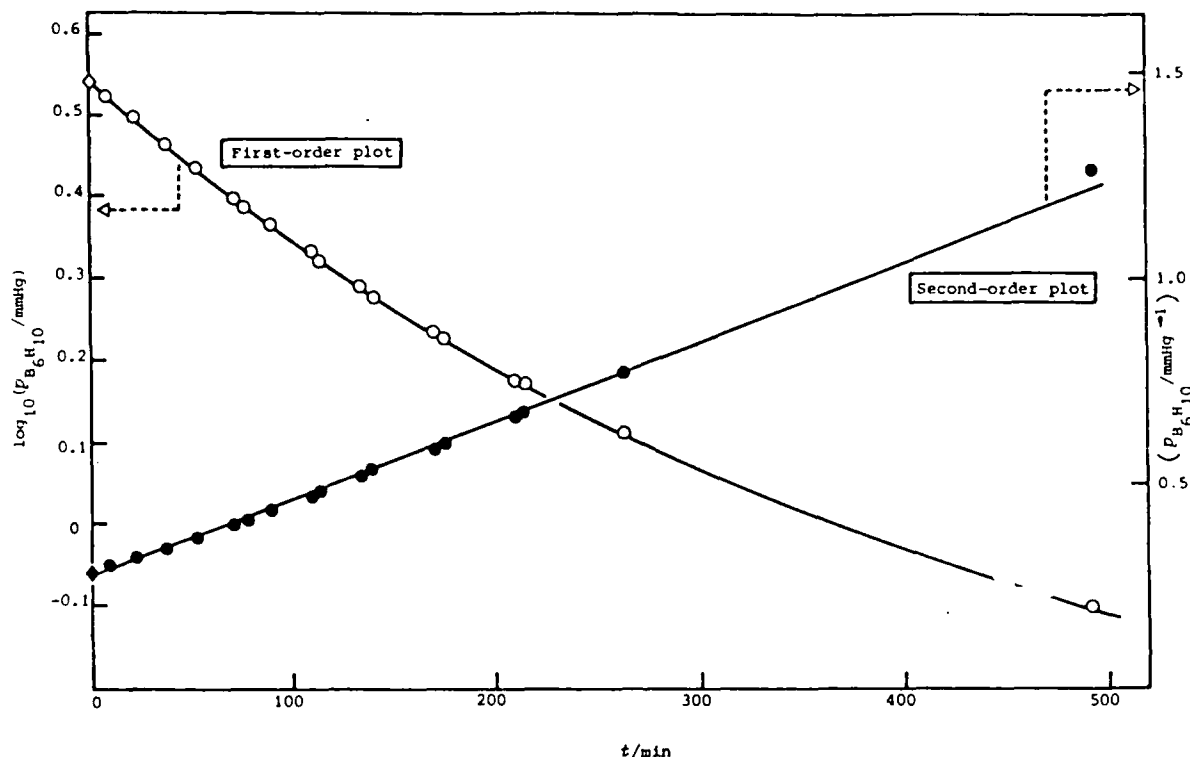


Figure 4. First- and second-order plots for the thermolysis shown in Figure 1.

hydrogen. To test this, additional experiments were carried out at 426 K in which hydrogen was added to the initial charge of  $B_6H_{10}$ . In one such experiment in which the initial pressure of hydrogen was 25 mmHg, the second-order rate constants for the initial production of hydrogen and consumption of  $B_6H_{10}$  were found to be  $78 \times 10^{-5}$  and  $68 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively, in good agreement with the average values of  $76.3 \times 10^{-5}$  and  $81.6 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for runs carried out at 426 K with no added hydrogen.

Mechanistic Conclusions.— From these various observations it seems likely that there are at least two reaction pathways involved in the thermolysis of  $B_6H_{10}$ : a major route leading to the non-volatile solid and hydrogen, and a minor route producing  $B_5H_9$  and  $B_{10}H_{14}$ . Because of the relatively high thermal stability of  $B_5H_9$  and  $B_{10}H_{14}$  at the temperatures used in this work, it seems likely that they are end products of the mechanism that leads to them, and not intermediates in the formation of the solid. The simplest mechanism consistent with these facts involves a rate-determining bimolecular collision, with rapid elimination of two molecules of hydrogen from the  $(B_{12}H_{20})^\ddagger$  activated complex to give  $\{B_{12}H_{16}\}$ , a hitherto unproposed reactive intermediate, which rapidly polymerizes in the presence of excess  $B_6H_{10}$ . Alternative modes of de-activation of the  $(B_{12}H_{20})^\ddagger$  complex (discussed in detail in Appendix 1) cannot be entirely eliminated as possible routes to the production of the solid, but the evidence suggests that they are less likely. They do, however, offer plausible routes for the production of the minor amounts of  $B_5H_9$  and  $B_{10}H_{14}$  that are observed.

Room-Temperature, Liquid-phase Decomposition of Hexaborane(10).— In a related experiment, ca. 0.3 g of  $B_6H_{10}$  was left at room temperature in a sealed 400 ml ampoule for 2 years. During this time the colourless mobile liquid turned through various shades of yellow and orange, becoming progressively more viscous, and finally ending up as an extremely hard orange-red solid. Measurement of the non-condensable gas formed during this process indicated that one mole of hydrogen was produced for every mole of  $B_6H_{10}$  consumed, strongly suggesting that the reaction is closely related to that in the gas phase. The solid was found to be soluble in deuteriotoluene, and was shown by  $^{11}B$  nmr to be mainly polymeric with small amounts of occluded  $B_5H_9$  and  $B_{10}H_{14}$  (Figure 5). Trace quantities of the known hydride  $B_{16}H_{20}$  were shown to be present by mass spectrometry.

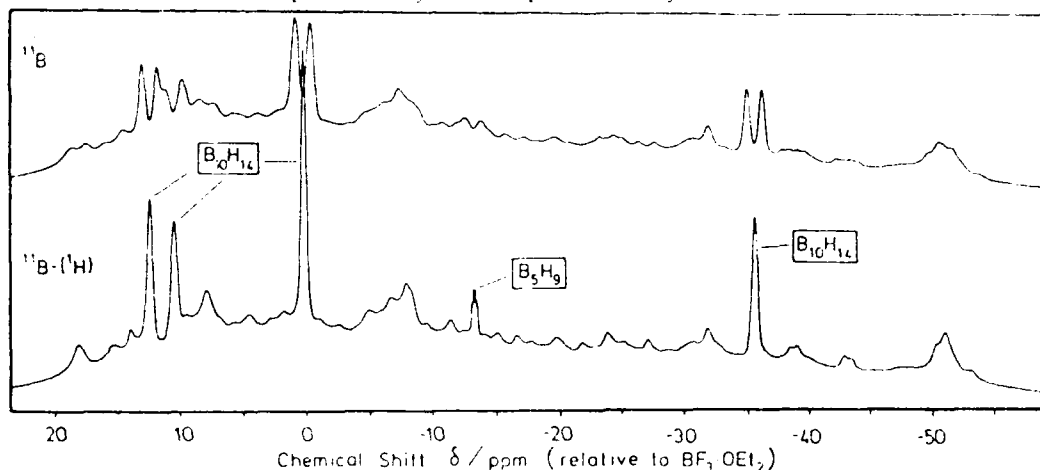


Figure 5. 128 MHz FT nmr spectra of the orange-red glassy solid produced in the room-temperature decomposition of neat hexaborane(10). Note the broad 'hump' underlying the sharp features of  $B_5H_9$  and  $B_{10}H_{14}$ , indicative of the presence of polymeric species.

Hot-Cold Reactions of Hexaborane(10).— If it is indeed formed, the intermediate  $B_{11}H_{14}$  would be the first known neutral dodecaborane. Attempts are therefore being made to isolate this or other possible stable intermediates by means of "hot/cold" (200°C/0°C) reactions of  $B_6H_{10}$ . So far, analysis of the products by high field  $^{11}B$  nmr (Figure 6) and mass spectrometry (solid probe) has failed

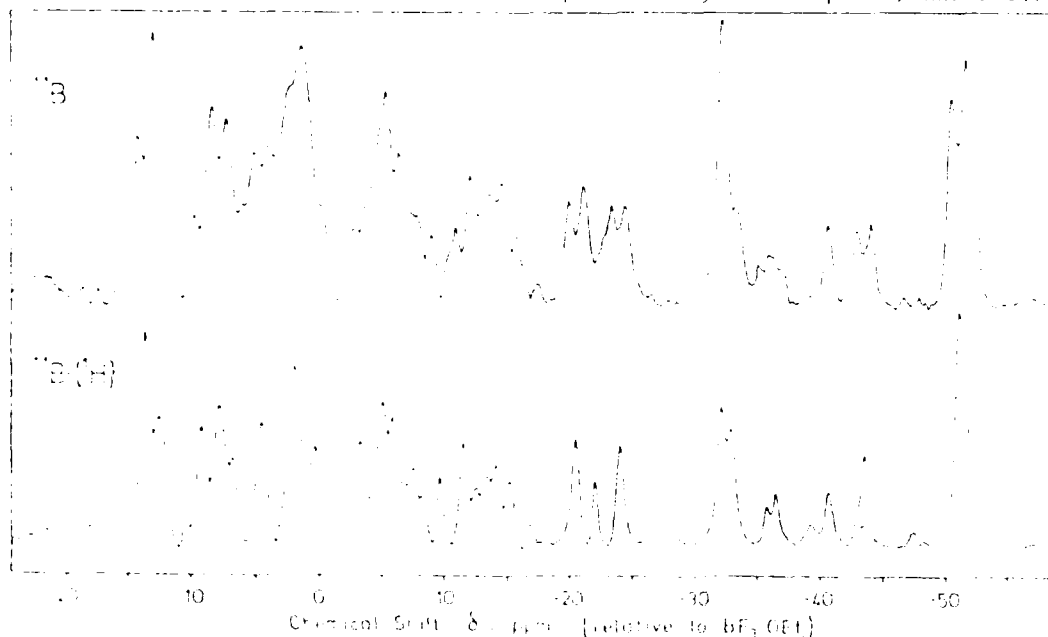


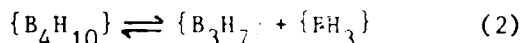
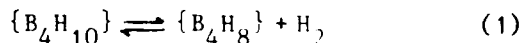
Figure 6. 128 MHz FT nmr spectra of products from hot/cold (200°C/0°C) reaction of  $B_6H_{10}$ . Note absence of any broad underlying features characteristic of polymeric species.

to detect any  $B_{12}$  species, but has shown that the known compounds  $B_{13}H_{19}$ ,  $B_{14}H_x$  ( $x = 18$  or  $20$ ),  $B_{15}H_{23}$ ,  $B_{16}H_{20}$ , and  $B_{18}H_{22}$  are all formed in the reaction - some in good yield. In the past 19 these compounds have been made only in extremely small amounts. We are therefore hopeful that this technique will provide a convenient route into the chemistry of these interesting higher boranes, for which only structural information is so far available. It is interesting to note that polymeric species are either absent entirely, or produced in only minor amounts under these conditions.

Deuterium Exchange with Hexaborane(10).- In an experiment in which  $B_6H_{10}$  (3.6 mmHg) and deuterium (25 mmHg) were held together in a clean glass bulb at room temperature for ~20 hours, no exchange was observed. Surprisingly, however, exchange occurs rapidly (at the basal terminal sites only) if the inner surface of the glass bulb is coated with 'polymeric' borane solids. This observation has not been noted previously, though exchange between  $B_6H_{10}$  and  $B_2D_6$  has been recorded by others. The present result suggests a convenient synthetic route to hexaborane(10) deuterated preferentially at the terminal basal sites, and further experiments are planned to assess the usefulness of this method.

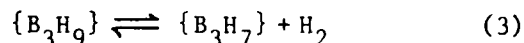
#### A Mass-Spectrometric Investigation of the Exchange of Deuterium with Tetra-borane(10) in the Gas Phase

Introduction.- The gas-phase thermolysis of  $B_4H_{10}$  has been the subject of numerous studies, though there is still disagreement in the literature about the steps involved in the initial stages of its decomposition. An early study <sup>20</sup> suggested that  $B_4H_{10}$  decomposes by two simultaneous first-order paths (1) and (2), leading to the formation of three highly reactive species  $\{B_4H_8\}$ ,  $\{B_3H_7\}$ , and  $\{BH_3\}$ .



Subsequent kinetic studies <sup>21,22</sup> strongly implicated  $\{B_4H_8\}$  as the reactive intermediate of prime importance, and there is ample indication of this from other experiments (see Appendix 3 for detailed references). However Koski <sup>23</sup> eliminated equilibrium(1) on the grounds that no exchange was observed between dideuterium and  $B_4H_{10}$  during a period of 130 minutes at  $45^\circ C$ . To resolve this worrying inconsistency we have therefore designed a careful series of experiments to establish unequivocally whether dideuterium exchanges directly with  $B_4H_{10}$  in the gas phase at moderate temperatures.

Results and Discussion.- Full technical details and experimental results are given in Appendix 3. It was shown conclusively that in a mixture of stoichiometry  $B_4H_{10} : 3D_2$  at  $42^\circ C$ , ca. 7% of the hydrogen atoms are replaced by deuterium in a period of 130 minutes. The possibility that the exchange might be occurring by an indirect or autocatalytic mechanism was eliminated by a series of experiments in which the rate of exchange was shown to be independent of small admixtures of the gaseous decomposition products  $B_2H_6$ ,  $B_5H_{11}$ , and the hexaboranes, and unaffected by the presence of polymeric borane deposits on the inner surface of the pyrex vessel. Moreover, the possibility that exchange might occur as a result of reaction (2) in conjunction with the postulated <sup>1</sup> reversible reaction (3) can be ruled out since reaction (3) is in fact the



rate-determining step in the decomposition of diborane which does not occur appreciably at temperatures below  $100^\circ C$ . If it did contribute to the exchange processes, then this would imply simultaneous and extensive decomposition of  $B_4H_{10}$ , which is not observed (at  $42^\circ C$ ). These considerations strengthen the

view that reaction (1) is of major importance in the thermal decomposition of  $B_4H_{10}$  and that this equilibrium plays a key role in borane interconversion reactions. The possible significance of reaction (2) in thermal decomposition at elevated temperatures is not excluded and detailed kinetic studies of the thermolysis of  $B_4H_{10}$  are in progress to gain further insight into the mechanism of its decomposition.

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